Plate-Based Fuel Processing System

R. A. Dalla Betta (Primary Contact), J. Barnes, C. Faz, T. Ho, H. Liu, J. Nicole, V. Sokolovskii, D. Yee
Catalytica Energy Systems
430 Ferguson Drive
Mountain View, CA 94043
Phone: (650) 940-6310; Fax: (650) 965-4345; E-mail: rdallabetta@CatalyticaEnergy.com

DOE Technology Development Manager: Donna Ho
Phone: (202) 586-8000; Fax: (202) 586-9811; E-mail: Donna.Ho@ee.doe.gov

Technical Advisor: Walt Podolski
Phone: (630) 252-7558; Fax: (630) 972-4430; E-mail: podolski@cmt.anl.gov

Objectives

- Develop reactor designs and catalyst systems for the direct steam reforming of gasoline to a hydrogen-containing stream adequate for a proton exchange membrane (PEM) fuel cell.
- Develop computer simulation models of these systems to predict and optimize performance.
- Develop and test prototype reactors in a 1 to 10 kW(e) size range and demonstrate DOE target performance, especially fast startup and load change.
- Demonstrate integrated fuel processor system operation.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- I. Fuel Processor Startup/Transient Operation
- J. Durability
- L. Hydrogen Purification/Carbon Monoxide Cleanup
- M. Fuel Processor System Integration
- N. Cost

Approach

- Develop conceptual plate reactor designs for steam reforming, water gas shift and preferential CO oxidation. Assemble detailed computer simulation models for these designs.
- Develop catalyst washcoat compositions with the required activity, selectivity and initial durability consistent with the catalyst performance requirements specified by the simulations. As required, measure detailed reaction kinetics for these catalyst compositions.
- Design and fabricate prototype plate reactor mechanical designs in the 1 to 10 kW(e) size range.
- Demonstrate plate reactor performance including startup, transient operation, efficiency and other performance factors.

Accomplishments

- Completed structural analysis of plate reactor system and established design criteria for required cyclic durability (startup and transient) and developed prototyping strategy for an initial laboratory

demonstration directed at transient and efficiency criteria. Proceeding with multiple parallel paths with future down-select to one or two final prototype units for demonstration.

- Developed and demonstrated a steam reforming catalyst with the required performance using the Argonne National Laboratory (ANL) Benchmark Fuel I with 10 ppm sulfur. Global kinetics have been measured for use in the plate reactor simulation model.
- Developed a base metal, non-pyrophoric water gas shift catalyst that is air stable and does not require pre-reduction. Demonstrated stability to 500 hours and activity meeting the DOE target performance.
- Developed a preferential CO oxidation catalyst that can achieve the required reactor performance for a plate configuration operating at 150°C. Demonstrated stability to 800 hours.

Future Directions

- Using measured kinetics for the best catalysts, complete simulation modeling for the target steam reforming plate reactor system. Complete prototype plate reactor designs for this reactor and fabricate at least one and possibly two prototype designs at the 1 to 10 kW(e) size for demonstration testing. Modify test rig facilities to accommodate the prototype units to accomplish testing including startup and transient operation over the required load range. Demonstrate startup to full load in less then 60 seconds and, if possible, less then 30 seconds, and demonstrate rapid transient load variation.
- Develop computer simulation models of the water gas shift reactor and preferential CO oxidation reactor designs using measured kinetics and design results from reformer prototype tests. Develop prototype plate reactor designs for these processes and fabricate prototype hardware for demonstration testing.
- Develop a transient simulation to demonstrate full fuel processor startup and transient operation consistent with DOE targets.

Introduction

The major obstacles to on-board reforming of liquid fuels to provide hydrogen for fuel cell applications are 1) time required for startup from a cold start; 2) ability to handle fast output transients; and 3) general complexity, size, weight and cost. These obstacles are being addressed in a number of DOE projects through development, integration and optimization of existing fuel processing system designs. This project is directed at investigating and developing plate reactor concepts where the catalytic function is integrated into a primary surface heat exchanger. The catalyst is coated onto the surface of a thin walled plate heat exchanger. For example, in the case of the steam reforming reactor, a reforming catalyst driving the endothermic reaction is coated on one side of the thin plate and a catalytic oxidation catalyst is coated onto the other side to drive the exothermic reaction, with the heat transferred efficiently between these catalysts by the thin metal plate. These structures can provide fast transient operation, compact reactors, very good temperature control and optimized operation. This project is directed at developing and demonstrating these reactor systems for processing gasoline to PEM-quality hydrogen.

Approach

The development of plate reactor designs for conversion of gasoline to hydrogen requires the integration of the detailed reactor design with details of the catalyst performance. To integrate all of these aspects and optimize the design, this project makes extensive use of reactor modeling that includes all important aspects of the system, e.g. convective gas flow, diffusion, catalyst layer structure, heat transfer throughout the structure and detailed kinetics of the catalytic reaction. Since in many cases reaction kinetics are not available, initial work was directed at developing catalyst materials with activity in the desired range that could be applied as a thin washcoat layer onto the plate surface. The kinetics of the catalytic reaction were then measured in sufficient detail to allow adequate modeling of the plate reactor

design using in-house developed computer codes for each reactor design. In many cases, improved catalysts were required and were developed.

The resulting target reactor design and catalyst system were then used to develop mechanical designs for a plate reactor to be used in laboratory demonstration at the 1 to 10 kW(e) size. Some early work was directed at understanding the effect of rapid temperature transients (startup, shutdown and loading) on the plate reactor design, and design aspects were identified that would lead to good cyclic life, particularly for the steam reformer reactor where the temperature transients are most severe.

Results

Steam Reforming: The defined approach is to directly steam reform gasoline in a plate reactor configuration using combustion on the opposite side of the plate to provide the endothermic heat of reaction. A catalyst has been developed that shows good activity and stability. Some test results are shown in Figure 1. Test conditions were:

- Temperature: 825°C, Pressure: 3.0 atm
- Space velocity (SV): 21.0 g fuel per g catalyst-hour
- Steam to carbon ratio: 3.8
- Fuel: ANL Benchmark Fuel I with 10 ppm sulfur
- Tube wall coated test reactor that simulates the required flow conditions, catalyst washcoat layer and catalyst temperature

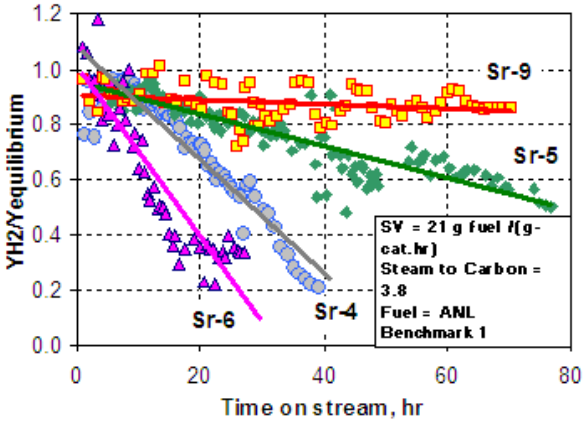

Figure 1. Steam Reforming of ANL Benchmark Fuel I with 10 ppm Sulfur on 4 Different Catalyst Materials under Plate Reactor Conditions

While pressure variation causes some fluctuations in the H_2 yield, the catalyst performance is relatively stable. The amount of catalyst required for a 50-kW(e) reactor is 0.42 kg, assuming the catalyst activity is stable at this performance level. Measurements are in progress to obtain a global kinetic expression for use in developing a detailed simulation of the plate reformer system. This catalyst will be incorporated into the demonstration prototype plate reformer described later.

Water Gas Shift Reactor: Catalytica Energy Systems Inc. (CESI) has developed an improved water gas shift catalyst (WGS) formulation with highly desirable characteristics such as 1) no pre-conditioning requirement, 2) no air sensitivity, 3) non-precious metal based, and 4) low sensitivity to condensed water. This catalyst has shown good durability (Figure 2) in reactor runs up to 500 hours. For this level of activity, 5 kg of catalyst would be required for a 50-kW(e) fuel processor, which meets the DOE WGS catalyst performance targets.

Durability data for WGS catalysts is very important due to the high sensitivity of this system to thermal degradation and past experience that durability is highly dependent on composition and operating conditions. For this reason, a static aging system is being developed to age the catalyst materials for long times, e.g. up to the target durability of 5000 hours, with minimum effort and cost. The strategy is to age a large batch of the target material at conditions that simulate water gas shift

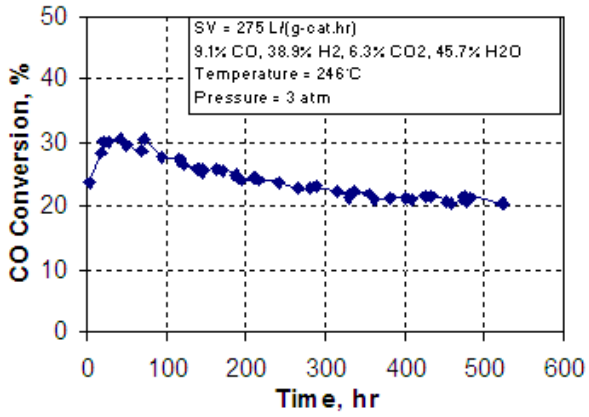

Figure 2. Water Gas Shift Reaction Durability Run with Base Metal Catalyst

reactor operation and periodically remove samples for characterization and activity testing. CESI has shown this to be a cost effective strategy for obtaining catalyst durability data. Work is currently in progress to validate this system by comparison of static aged catalyst materials with materials aged in the laboratory bench-scale test reactor as presented in Figure 1. New catalyst compositions will be similarly aged to determine long-term durability.

Detailed kinetics have been measured for these stable base metal water gas shift catalysts, and these data are being used to model plate reactor designs for optimum operation. As an example, the plate reactor configuration using countercurrent air as the temperature control media with the catalyst materials developed in this program provides greater then 90% CO conversion with a typical steam reformer outlet composition and a catalyst loading of 3 kg, as shown in Figure 3. While this shows the potential performance of such a system, catalysts with durability at higher temperatures (340 to 380°C) must be developed.

Preferential Oxidation: The plate reactor approach allows the close control of catalyst temperature during reaction. This is especially important for the preferential oxidation of CO, where the selectivity of the reaction is highly temperature dependent. Testing with a packed bed reactor was unsuccessful due to this temperature dependence, and work was shifted to a wall coated test reactor design where the catalyst temperature could be controlled. Preliminary catalyst development is complete, and kinetics have been obtained over a wide range of operating conditions. Durability test results are shown in Figure 4, where a fresh catalyst and an aged catalyst are compared. The catalyst was aged by operation in preferential oxidation reaction, including kinetic measurements and long-term runs at conditions simulating low load to high load and low conversion to high conversion. Test conditions are:

- Inlet gas composition: 1% CO, 1% O_2, 64% H_2, 18% H_2O, 16% CO_2
- Gas space velocity: 118 liters/gcat-hr

The performance of the aged catalyst is essentially identical to the fresh material. One unusual aspect of this catalyst is the observation that the selectivity for oxidation of CO compared to oxidation of H_2 was observed to vary from 50 to 60% over most conditions. The amount of catalyst required for a 50-kW(e) preferential oxidation reactor in the plate configuration is about 600 g when operated at 150°C and achieving 20 ppm CO in the outlet gas stream.

Demonstration Prototype Plate Reformer: One of the major issues in the design of a plate reactor

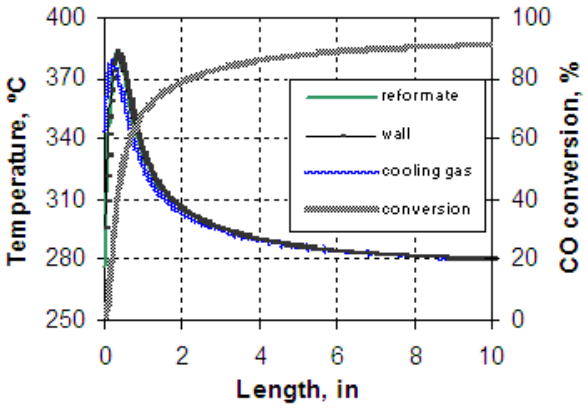

Figure 3. Model simulation of water gas shift plate reactor design with countercurrent cooling gas flow. CO conversion of 90% achieved with 3 kg of catalyst if activity can be maintained over these conditions.

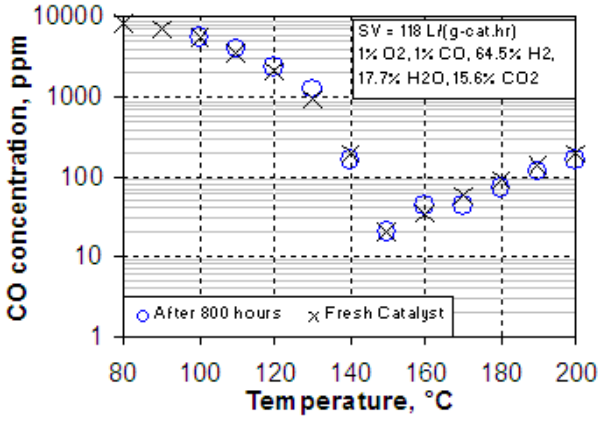

Figure 4. Catalyst durability demonstration for the preferential oxidation of CO. CO conversion as temperature was varied from 80 to 200°C for a fresh and 800 hour aged catalyst. No catalyst deactivation was observed.

system is the high stress level arising from the startup and transient cycles that produce large temperature transients and large thermal gradients. Previously reported work described extensive finite element structural analysis of the plate reactor concept and examined numerous reactor design approaches. A design approach was developed that resulted in a calculated maximum strain of 0.28%, close to the target value that would provide the required cyclic fatigue life for the rapid thermal transients occurring during startup and load following. This design approach was used to develop three approaches to a prototype reactor mechanical design for fabrication and demonstration testing. Typical design aspects of the prototype will be:

- Primary surface plate thickness: 0.15 mm
- Catalyst washcoat layer thickness: 20 to 50 microns
- Gas flow channel dimensions: 0.6 to 1.5 mm diameter by 100 mm

The manifolds supplying the feed (fuel and air to the combustion side, fuel and steam to the reformer side) are sized to ensure uniform distribution (within 4%) of the feed to all of the plates. The plates and manifold are assembled in a manner to minimize thermally induced stresses.

The new design is being taken to prototype fabrication through 3 parallel approaches: (1) using pre-existing heat-exchanger plates that provide most of the required functionality, (2) using soft-tooled plate stamping to produce an a priori design and (3) using a fin-folding technique to produce a design derived from gas turbine heat exchangers that show good transient performance. At least one but most likely two of the fabrication approaches will be selected to produce a prototype unit in the 1 to 10 kW(e) range for demonstration testing.

Conclusions

- Computer simulation has demonstrated that plate reactor designs provide very efficient reactor performance for steam reforming, water gas shift and preferential CO oxidation arising from the ability to control the catalyst temperature to a desired range.
- Catalyst systems have been developed that can be applied as a washcoat onto heat exchange surfaces and can provide the required performance for plate reactor fuel processor systems.
- Direct steam reforming of gasoline with 10 ppm sulfur has been demonstrated. The gasoline plate reformer would be the first reactor in a fuel processor, and a design approach has been developed to demonstrate startup including fast startup and transient operation. Design and fabrication of prototype plate reactors is in progress.

FY 2003 Publications/Presentations

1. J. M. Zalc, H. Liu, R. Dalla Betta; "System Integration Issues for a Plate Reactor-Based Automotive Fuel Processor", Am. Institute of Chemical Engineers Meeting, 8 November 2002, Indianapolis, IN.

2. "Plate Based Fuel Processing System", FreedomCAR Technical Team Review, 19 March 2003, Detroit, MI.

3. V. Sokolovskii, J. Zalc, D. Poojary, T. Ho, D. Taube, G. Malukhin, R. Dalla Betta; "Non-noble Metal Water-Gas Shift Catalysts for Automotive Fuel Cell Application", American Chemical Society Meeting, April 2003.

4. "Plate Based Fuel Processing System", 2003 DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program Review Meeting, 19-22 May 2003, Berkeley, CA.